CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY
DEPARTMENT OF TOXIC SUBSTANCES CONTROL
Final Decision to Certify
Hazardous Waste Environmental Technologies

The California Environmental Protection Agency, Department of Toxic Substances Control (DTSC) intends to certify the following company's hazardous waste environmental technology:

Applicant: U.S. Army Environmental Center
SFIM-AEC-ETD, Bldg. 4430
Aberdeen Proving Ground, Maryland 21010-5401

Technology: Tri-Service Site Characterization and Analysis Penetrometer System with Hydrosparge VOC Sensor

Chapter 412, Statutes of 1993, Section 25200.1.5., Health and Safety Code, enacted by Assembly Bill 2060 (AB 2060 by Assemblyman Ted Weggeland) authorizes DTSC to certify the performance of hazardous waste environmental technologies. The purpose of the certification program is to provide an in-depth, independent review of technologies at the manufacturers' level to facilitate regulatory and end-user acceptance. Only technologies that are determined to not pose a significant potential hazard to the public health and safety or to the environment when used under specified operating conditions may be certified. Incineration technologies are explicitly excluded from the certification program.

DTSC makes no express or implied warranties as to the performance of the manufacturer's product or equipment. The end-user is solely responsible for complying with the applicable federal, state, and local regulatory requirements. Certification does not limit DTSC's authority to require additional measures for protection of public health and the environment.

By accepting certification, the manufacturer assumes, for the duration of certification, responsibility for maintaining the quality of the manufactured equipment and materials at a level equal to or better than was provided to obtain certification and agrees to be subject to quality monitoring by DTSC as required by the statute under which certification is granted.

DTSC's proposed decision to certify was published on October 20, 2000 in the California Regulatory Notice Register 2000, Volume No. 42-Z, pp.1706-1712. DTSC’s Final Certification shall become effective on January 15, 2001. Additional information supporting DTSC's final decision is included in the **October 2000** Draft Final Certification Evaluation Report, available at:

California Environmental Protection Agency
Department of Toxic Substances Control
Office of Pollution Prevention and Technology Development
P.O. Box 806
1001 I Street, 12th Floor
Sacramento, California 95812-0806
Attn: Dr. Bruce La Belle (916) 322-3670

A description of the technology to be certified, the certification statement and the certification conditions and limitations for the technology of the company listed above follows.

CERTIFICATION PROGRAM (AB 2060) FOR HAZARDOUS WASTE ENVIRONMENTAL TECHNOLOGIES

FINAL NOTICE OF TECHNOLOGY CERTIFICATION

Technology: Tri-Service Site Characterization and Analysis Penetrometer System with Hydrosparge VOC Sensor

Manufacturer: U.S. Army Environmental Center
SFIM-AEC-ETD, Bldg. 4430
Aberdeen Proving Ground, Maryland 21010-5401

Background

The Tri-Service Site Characterization and Analysis Penetrometer System (SCAPS**)** Hydrosparge (HS) VOC Sensor is a near real-time in-situ subsurface screening method for volatile organic compounds (VOCs) in groundwater. The technology was developed by the U.S. Army Corps of Engineers Waterways Experiment Station through the Tri-Service SCAPS program and is one of a planned family of sensors collectively called the Site Characterization and Analysis Penetrometer System, or SCAPS, that will combine remote sensors with a cone penetrometer platform to provide rapid, in-situ, subsurface measurements of many different contaminants.

The conventional or traditional approach to characterizing groundwater contamination plumes depends on the installation of monitoring wells and collection of water samples followed by laboratory analyses, is usually a slow, iterative, and costly process. Significant delays occur in site characterization while samples are analyzed and new monitoring wells are being installed and developed. The SCAPS HS technology was designed to improve upon conventional site characterization by providing rapid qualitative to semi-quantitative information about the subsurface distribution of volatile organic contamination in groundwater.

Technology Description

The SCAPS Hydrosparge VOC Sensor consists of an in-situ sparge module interfaced to an ion trap mass spectrometer (ITMS) to provide near real-time semi-quantitative field screening analyses of volatile organic compounds (VOCs) in groundwater. The Hydrosparge VOC Sensor was developed for deployment with a standard cone penetrometer (CP) platform using a direct push groundwater sampling tool to create a temporary groundwater sampling point. The CP is used to push the commercially available Hydropunch™ or Powerpunch™ groundwater sampling tool to the desired depth. The CP push rods are then retracted, exposing a well screen to create a temporary sampling point. Before the in-situ sparge module is lowered into the temporary sampling point, groundwater is purged until pH, dissolved oxygen, temperature, and conductivity remain constant and the groundwater level has been allowed to stabilize. The Hydrosparge VOC Sensor is then lowered into the well through the push rods to approximately 18 inches below the groundwater surface. The hydrosparge module uses helium gas at a calibrated flowrate to purge VOC analytes from the groundwater and to transfer the analytes via teflon tubing directly into an ITMS on-board the SCAPS truck for real time analysis.

The hydrosparge module consists of an extraction chamber, a conductivity meter, a helium purge tube, and a sample transfer line. Groundwater enters the extraction chamber from an opening at the base of the hydrosparge module. The conductivity meter in the extraction chamber ensures that an air/water interface is maintained. VOCs are sparged from the groundwater with helium at a calibrated flow rate through the purge tube. The helium and VOC vapors then exit the extraction chamber via a Teflon tube at the top which is connected to the ITMS.

The ITMS is comprised of a quadruple ion-trap mass spectrometer, a capillary restrictor interface, and a sample inlet designed for use with the HS for on-site measurement and monitoring. Analysis of the HS samples is performed with the use of a Teledyne 3DQ ITMS or Finnigan ITMS 40 operating in the electron impact mode or chemical ionization mode. The ITMS is directly fitted to a 20 cm DB-5 capillary column with restrictor heated interface operated at 105EC. The capillary interface limits flow into the ITMS at 0.1 to 1.0 mL/min., which is compatible with both electron ionization (EI) and chemical ionization (CI) sources. The ITMS is operated in a full scan mode from masses 40 to 250 amu. Unlike most mass spectrometry systems, the analyte vapors are directly subject to mass spectrometry without prior separation. Therefore, analyte identification is performed entirely by means of mass ion identification. Analytes with the same quantitation mass ions cannot be distinguished from each other and are reported as totals similarly to analytes co-eluting in GC techniques.

Since the ITMS does not have a separation mechanism other than the ion-trap mass spectrometer itself, compounds which produce identical primary characteristic ions, or positional and geometric isomers (e.g., 1,1-dichloroethene and 1,2-dichloroethene), cannot be positively identified by this system unless a characteristic secondary ion is available for monitoring. Compounds with higher molecular weights may produce the same fragment ions which will increase the signal of target analytes. A false positive result may occur when there are VOCs present in the sample which yield molecular ions or ion fragments with the same mass/charge (m/z) values as the characteristic ions of the target VOCs. Therefore, this detection system can only be used to detect or to confirm the presence of target analytes but not for the positive identification of unknown compounds.

Although the sensor provides a nearly linear numerical response over a dynamic range of approximately three orders of magnitude starting from a minimum detection capability as low as 1 Fg/L, the certification is limited to a qualitative to semiquantitative field screening method because the effectiveness of hydrosparging is site specific, and may vary as a function of the analytes being investigated.

Details of the analytical method for in-situ measurement of VOCs in groundwater with SCAPS HS are described in the document, "Direct Sampling Ion-Trap Mass Spectrometry for the Measurement of Volatile Organic Compounds in Water, Soil and Air," Draft EPA SW-846 Method 8265, 1997. The draft Method 8265 identifies 30 target analytes and their corresponding quantitation ions that can be analyzed by ITMS. The organic work group of U.S. EPA is now considering Method 8265-Volatiles by Direct Sampling Ion-Trap Mass Spectrometry (ITMS) for inclusion in the Update IV B of EPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods.

The evaluation focused on the use of the Hydrosparge VOC Sensor, including both the in-situ sparge module and the on-board ITMS, for near real-time analysis of selected VOCs in groundwater. The use of direct push sampling points for field screening purposes is a generally accepted practice, and therefore was not evaluated. The evaluation specifically did not address the use of direct push sampling points for obtaining representative groundwater samples, nor did it address any other uses of the CP system. The evaluation report for this technology provides a more detailed description of the CP platform and the direct push groundwater sampling tools that were used in the field studies conducted for this certification evaluation.

Basis for Certification

The Hydrosparge module operation is based on Henry's Law where for low concentrations of low-solubility VOCs in water, the concentration of the VOC in the gas phase is proportional to the concentration in the water phase. For the sparge gas flowrate used in the Hydrosparge module, the VOC concentrations in the water phase remain relatively constant over the measurement time period. The purged VOCs are transferred directly to the ion-trap mass spectrometer for analysis.

The technology evaluation focused on the comparison of field results with those obtained using accepted reference methods for groundwater analyses. The performance parameters used to evaluate the technology included sensitivity, specificity, precision, accuracy, and reliability.

Since the SCAPS HS is considered a field screening technology, performance was primarily evaluated in terms of the potential for false positive and false negative results. Occurrences of false positives and negatives were determined based on results for the in-situ SCAPS HS analyses versus the analyses by reference method, EPA Method 8260B. For field screening technologies, performance is generally considered acceptable if there are fewer than 5% false negatives and fewer than 5% false positives. Of particular concern is the occurrence of false negatives, that is the event of determining a sample is clean or uncontaminated when it is not. Failure to detect a contaminant that is present could have an adverse impact on site or public health management decisions.

The data for the individual field studies were evaluated based on data distribution and data correlation with the reference method. Reported detection limits for all of the analytes were similar for both the SCAPS HS method and reference method (EPA Method 8260B), which were 5 µg/L except for the analytes reported at the Massachusetts Military Reservation site which had detection limits of 1 µg/L. For data distribution, an analytical method's performance is typically evaluated over a range of concentrations of two or more orders of magnitude. Therefore, linear correlations were not calculated for analytes that were not detected over a range of concentrations of two or more orders of magnitude. Field and reference method results were considered to correlate well if the correlation coefficient was greater than or equal to 0.80 ($R^2 \geq 0.80$).

Previous field demonstrations and technology development efforts conducted from May 1995 through June 1997 at NAS Whiting Field, Aberdeen Proving Grounds, and the Massachusetts Military Reservation were reviewed. At the Aberdeen Proving Grounds, one field study was conducted at Building 525 while another field study consisting of two demonstrations approximately 3 months apart was conducted at the Bush River Study Area (BRSA). These field studies involved the installation of more than 126 temporary wells and the analyses of 126 groundwater samples collected using the SCAPS HS method and conventional groundwater sampling techniques, respectively. The U.S. Army Corps of Engineers (USACE) conducted these studies without DTSC oversight and provided only summary data for DTSC review.

For the certification evaluation, the USACE Waterways Experiment Station conducted field studies at two locations in different geographic areas with different site conditions and contaminant concentrations. The New Jersey Department of Environmental Protection provided oversight for the field study conducted at Fort Dix. OPPTD staff were involved in the review of field demonstration plans prior to conducting the field study for the Davis Global Communication Site (DGCS). At the DGCS, two field demonstrations were conducted within 4 months of each other. Detailed QA/QC data packages were submitted for field studies completed at Fort Dix and the DGCS. OPPTD observed operations and technology validation procedures in the field during the demonstrations conducted at the Davis site.

For QA/QC purposes, splits of selected verification samples were analyzed by an independent laboratory for the November/December 1996 DGCS field demonstration and the Fort Dix field study. DTSC Hazardous Materials Laboratory staff reviewed the data packages for the results of these quality control samples which were analyzed by West Laboratory for the Davis site, and PDP for the Fort Dix site. For the Davis site, comparison of the Hydrosparge and USACE Environmental Chemistry Branch (ECB) results showed good data correlation (R^2=0.9) while the West Laboratory results correlated poorly with the Hydrosparge and ECB results. The Fort Dix split results contained insufficient data points for each analyte to perform a regression analysis but the results appeared to be comparable for the three methods.

Data generated from all the field studies were analyzed for false positives, false negatives, and correlation coefficients individually and pooled by analyte. A summary for the analytes certified in this notice is provided below. A discussion on each field study and their results is presented in the evaluation report.

When pooled, the concentrations for trichloroethene (TCE), dichloroethene (DCE), perchloroethylene (PCE), benzene, toluene, xylene, and carbon tetrachloride were distributed over a range of at least two orders of magnitude. Depending on the analyte, the sample concentration distribution was 55-79% for concentrations below the detection limit, 4-264% for concentrations between the detection limit and 100 µg/L, and 5-20% for concentrations over 100 µg/L.

Pooled data for TCE, benzene, and carbon tetrachloride met the criteria of less than 5% false positives and negatives and had good correlation ($R^2 \geq 0.80$). Pooled data for PCE, toluene, and xylenes met the criteria of less than 5% false positives and negatives but had poor correlation ($R^2 < 0.80$). Pooled data for DCE met the criteria for less than 5% false positives and had good correlation ($R^2 \geq 0.80$) but did not meet the criteria of less than 5% false negatives. Two DCE false negatives could be considered true positives since the SCAPS HS method provided estimated values which would reduce the false negatives to 5%.

For individual field studies and demonstrations, the percentage of false positives and negatives for xylenes, benzene, and carbon tetrachloride were less than 5% but had poor correlations ($R^2 < 0.80$). For TCE, DCE, and PCE, a few field studies had false positives and negatives which exceeded the 5% criteria and had correlations which varied from poor ($R^2 < 0.80$) to good ($R^2 \geq 0.80$). For toluene, false positives and negatives were below the 5% criteria but correlations varied between poor ($R^2 < 0.80$) to good ($R^2 \geq 0.80$).

Several other factors were also considered in the interpretation of the data. One of these factors was the data distribution. For four of the eight field studies reviewed, the data consisted of less than 20 points where one false positive or negative would cause the percentage of false positives or negatives to exceed 5%. For all the field studies, the pooled data for each analyte contained a large number of data points where the concentration was below the detection limit. With the large number of data points grouped near the origin, the data distributed at higher concentrations were shown to have a greater influence on the correlation coefficient.

Another factor considered was the technology’s inability to produce consistent results for a specific analyte at the same location. This was illustrated in the differing correlations presented for demonstrations conducted at the DGCS and the Aberdeen Proving Grounds BRSA (see evaluation report for details). Since field notes on operator field activities and site conditions were not available in the summary reports, OPPTD staff were unable to assess potential effects of these parameters on the results. Differences in the consistency of the SCAPS HS method to report groundwater concentrations between demonstrations could be due to site conditions, personnel operating the SCAPS HS, helium flow rate used in well sparging, and equipment cleaning and calibration methods used. These factors may contribute to inconsistent results for the same site between demonstrations.

Certification Statement

Under the authority of Health and Safety Code section 25200.1.5, the Site Characterization and Analysis Penetrometer System Hydrosparge VOC Sensor (SCAPS HS) is hereby certified as a hazardous waste **Site Characterization** technology subject to the specific conditions including the limitations/disclaimer set forth in the Certification Notice as published in the California Regulatory Notice Register on December 15, 2000 Register No. 2000, Volume No. 50-Z, pages 2138 - 2144. The SCAPS HS is certified as a near real-time in-situ field screening method for trichloroethene (TCE), benzene, carbon tetrachloride, perchloroethylene (PCE), dichloroethene (DCE), toluene, and xylenes in groundwater. For TCE, benzene, or carbon tetrachloride, the technology was demonstrated to meet the criteria of less than 5% false positives and negatives and had good correlation ($R^2 \geq 0.80$) and is certified as a qualitative to semi-quantitative field screening method for these analytes. For PCE, toluene, and xylenes, the technology was demonstrated to meet the criteria of less than 5% false positives and negatives but had lower correlations ($R^2 < 0.80$) and is certified as a qualitative field screening technology for these analytes. For DCE, the technology was demonstrated to have good correlation ($R^2 \geq 0.80$) but did not meet the criteria of less than 5% false negatives and is certified as a qualitative field screening technology for this analyte. The technology has applicability to other VOCs which can be detected with an ion-trap mass spectrometer (ITMS), provided these compounds can be effectively sparged from the groundwater with SCAPS HS. As a field screening method, SCAPS HS can be used to further delineate the movement and distribution of groundwater contamination at a site and is a means to optimize the placement of additional permanent monitoring wells. Detection thresholds for all analytes achieved in field studies using SCAPS HS are comparable to those of the reference method. SCAPS HS has applicability to field screening for the presence of known contaminants, and the identification of an unknown substance when ions uniquely characteristic to those substances are present. Isomers such as 1,1-DCE and 1,2-DCE or other compounds which produce the same quantitation mass ions cannot be distinguished from each other with this method. False positive or high results may occur when there are VOCs present in the sample which yield molecular ions or ion fragments with the same m/z values as the characteristic ions of the target VOCs.

Limitations of Certification

DTSC makes no express or implied warranties as to the performance of the SCAPS Hydrosparge VOC Sensor. Nor does DTSC warrant that the SCAPS Hydrosparge VOC Sensor is free from any defects in workmanship or materials caused by negligence, misuse, accident or other causes. However, DTSC believes that the SCAPS Hydrosparge VOC Sensor can be used in accordance with the conditions specified in this certification notice to achieve the results specified herein.

This certification is subject to the regulations found in Title 22 of the California Code of Regulations (CCR 22), Chapter 46, Section 68000, which include the duration of the Certification, the continued monitoring and oversight requirements, and the procedures for certification amendments and decertification.

Use of the certified technology is limited to field screening for detection or confirmation of target analytes, but not for positive identification of analytes. Since the ITMS does not have a separation mechanism other than the mass spectrometer, compounds which produce identical primary characteristic ions, or positional and geometric isomers (e.g., 1,1-dichloroethene and 1,2-dichloroethene), cannot be positively identified by this system unless a characteristic secondary ion is available for monitoring. Compounds with higher molecular weights may produce the same fragment ions which will increase the signal of target analytes. A false positive result may occur when there are VOCs present in the sample which yield molecular ions or ion fragments with the same m/z values as the characteristic ions of the target VOCs.

Specific Conditions

1. Applicability. This certification is limited to use of the SCAPS Hydrosparge VOC Sensor for in-situ analyses of trichloroethene (TCE), benzene, carbon tetrachloride, perchloroethylene (PCE), dichloroethene (DCE), toluene, and xylenes. The technology may also be applied to the analysis of other chlorinated solvent compounds listed as target analytes in draft Method 8265, provided it can be demonstrated with confirmation sample analyses that these compounds are effectively sparged from the groundwater being investigated and detected by the on-board ITMS system.

2. Use for Groundwater. This certification is limited to use of the SCAPS Hydrosparge VOC Sensor in groundwater. Prior to SCAPS Hydrosparge analysis of groundwater in the temporary well or sampling point, the groundwater in the sampling point shall be purged until pH, dissolved oxygen, temperature and conductivity remain constant, and the groundwater level has been allowed to stabilize.

3. Operational Procedures. The SCAPS Hydrosparge VOC Sensor shall be operated in accordance with specific procedures developed by the U.S. Army Corp of Engineers Waterways Experiment Station and described in the following two documents: (a) Draft Method 8265, Direct Sampling Ion-Trap Mass Spectrometry for the Measurement of Volatile Organic Compounds In Water, Soil, and Air, SW-846 Organic Methods Workgroup, Revision WG 2, July 1997, and (b) Field Screening of VOCs in Groundwater using the Hydrosparge VOC Sensor, submitted to Current Protocol in Field Analytical Chemistry, John Wiley & Sons, Inc. prepared by William M. Davis, John S. Furey, and Beth Porter, 1998. The final version of Method 8265 accepted into SW-846, or any revisions made to the draft method as part of the SW-846 acceptance process, shall supersede the draft method referenced above.

4. Confirmation Samples. Confirmatory laboratory analyses of groundwater samples by EPA Method 8260B or equivalent **are required.** For this purpose, representative groundwater samples of the aquifer being investigated shall be collected and analyzed. This requirement is necessary to assess the applicability of the technology to identify specific contaminants present at the site. Different compounds may produce the same characteristic ions which are detected and quantified by the ITMS. Thus, the certified technology is only able to detect or confirm the presence of known specific contaminants. In addition, matrix effects, and even the particular contaminant or contaminants present, may vary with depth. The depth and size of the contaminant plume, and contamination profile of a site should all be considered in a site-specific sampling plan for determining the necessary number and locations of confirmation samples. Site characterization data obtained during prior investigations should also be considered for this requirement.

5. Direct Push Well Abandonment. The user shall comply with all applicable state and local regulations regarding the proper abandonment of direct push wells and push holes (i.e., well abandonment requirements). At a minimum, each direct push well shall be grouted from the bottom up using a cement bentonite slurry immediately after groundwater sampling is completed. The specific grout mixture used shall be documented at each site so future investigations or monitoring programs can anticipate the potential for detecting low concentrations of any additives and possible breakdown products. Additionally, water used in the grout mixture and in the grouting process shall be a water of known and documented quality. Examples of the USACE standard operating procedures for abandoning temporary groundwater sampling wells are available in the evaluation report.

6. Probe Cleaning. The steam cleaning system integral to the truck should be used to automatically steam clean the penetrometer rod sections as they are being withdrawn from the push hole and prior to being handled by the field crew and placed onto the storage racks. Spent water from the cleaning process, directed to a storage drum, should be properly classified and managed.

7. Compliance with Worker Health and Safety Laws. Operation of the SCAPS Hydrosparge VOC Sensor must be in compliance with all federal, state and local regulations relating to the protection of worker health and safety. In California these include, but are not limited to, Cal-

OSHA and OSHA requirements.

8. Personnel Training. Operators with chemical and analytical knowledge and proper training are required to use this technology. Training includes safe operation and maintenance of the Hydrosparge VOC Sensor, the cone penetrometer platform, the Hydrosparge module and associated sample collection equipment, and the ITMS analytical instrument.

9. Compliance with Applicable Federal, State, Local Regulations. The user shall comply with all applicable federal, state, and local regulatory requirements.

10. Modifications and Amendments at the Request of the Applicant. Modifications and amendments to this certification may be requested by the applicant and will be subject to approval by DTSC.

11. Certification Reference. The holder of a valid hazardous waste environmental technology certification is authorized to use the certification seal (California Registered Service Mark Number 046720) and shall cite the certification number and date of issuance in conjunction with the certification seal whenever it is used. When providing information on the certification to the user of the technology or another interested party, the holder of a hazardous waste environmental technology certification shall at a minimum provide the full text of the final certification decision as published in the California Regulatory Notice Register.

12. The user of the certified technology shall maintain adequate records to document compliance with the conditions of certification. The records shall be maintained onsite and available for inspection.

Regulatory Implications

This certification is for the specific claims, conditions, and limitations outlined in this notice, and is based on DTSC's evaluation of the technology's performance. The Certification does not change the regulatory status of SCAPS HS technology; it should, however, facilitate and encourage the acceptance of this technology as a field screening method for site characterization, thereby reducing the required number of monitoring wells, as well as the overall time and effort, required to fully characterize the migration and distribution of groundwater contaminant plumes at a given site.

Use of this technology as a field screening method for site characterization does not require a hazardous waste management permit issued by DTSC. However use of the technology may be subject to regulation by other state and local agencies. For each specific application, the end-user must ensure compliance with all applicable regulations and standards established by other state and local agencies.

This Certification is issued under the California Environmental Technology Certification Program, and is therefore subject to the conditions set out in the regulations, such as the duration of the Certification, the continued monitoring and oversight requirements, and the procedures for certification amendments, including decertification.

By accepting this Certification, the manufacturer assumes, for the duration of the Certification, responsibility for maintaining the quality of the manufactured materials and equipment at a level equal or better than was provided to obtain this Certification and agrees to be subject to quality monitoring by DTSC as required by the law, under which this Certification is granted.

Duration of Certification

This certification will remain in effect for three years from the date of issuance, unless it is amended or revoked for cause.